ENGLISH TRANSLATION
OF INTERNATIONAL APPLICATION
WO 95/13350 PCT/EP94/03618

An additive for the washing of glass bottles and its use for reducing glass corrosion

This invention relates to a new additive for aqueous alkaline solutions for bottle washing machines for washing glass bottles, more especially beverage bottles. The function of the additive is to reduce the corrosion of glass which normally occurs under alkaline bottle washing conditions. The invention also relates to the use of the additive in aqueous solutions for the machine washing of glass bottles.

Before reusable beverage bottles of glass are refilled, the labels have to be removed and the bottles thoroughly washed. Highly alkaline detergent solutions containing sodium hydroxide are normally used for this purpose in the bottle washing machines of bottling factories. The alkali metal hydroxide content is normally in the range from 0.5 to 5% by weight and more especially in the range from 1 to 3% by weight. Providing suitable products and processes are used, the required cleaning effect is achieved. An unwanted effect in bottle washing is corrosion of the glass. This is a phenomenon by which the surface of the glass bottles is chemically attacked, resulting in surface roughness. Secondary phenomena often include difficulties in cleaning the rough surface and the danger of microorganism growth in cracks and holes in the surface. It is known from practical experience and from laboratory tests that the corrosiveness of the cleaning solutions containing sodium hydroxide is increased by an increased percentage content of sodium carbonate.

Since the number of possible refilling cycles for reusable glass bottles is limited inter alia by the corrosion of glass during the cleaning process, there is

a need for additives which reduce the corrosion of glass in cleaning solutions. Accordingly, the problem addressed by the present invention was to provide a combination of active substances for aqueous alkaline cleaning solutions for the machine washing of glass bottles which, in addition to enhancing the cleaning properties, would contribute towards reducing glass corrosion.

Another problem addressed by the present invention was to formulate this combination of active substances as a concentrate which could be added in situ to the aqueous alkaline cleaning solution.

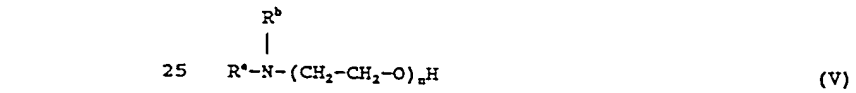
Aliphatic hydroxymono-, hydroxydi- or hydroxytricarboxlyic acids containing 3 to 6 carbon atoms and 1 to 5 hydroxy groups are known as components of industrial detergents. It is also known that geminal diphosphonic acids corresponding to general formula (I) below, aminomethylene phosphonic acids corresponding to general formula (II) below or phosphonocarboxylic acids corresponding formula (III) below can be added to cleaning solutions. It is assumed that the acids mentioned or rather their anions have complexing properties, especially towards the ions responsible for the hardness of water. In addition, the phosphonic and phosphonocarboxylic acids mentioned show so-called scale-inhibiting properties.

DE-C-23 25 829, for example, describes a sequestering agent for divalent and trivalent cations in the form of a mixture of 1-hydroxyethane-1,1-diphosphonic acid, aminotrimethylene phosphonic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid or water-soluble salts thereof. This document contains details as to which geminal diphosphonic acids, aminomethylene phosphonic acids and phosphonocarboxylic acids may be used as the combination of sequestering agents. The phosphonic acids mentioned in this document, which is hereby included as part of the disclosure of the present invention, are also suitable as

phosphonic acid components for the purposes of the present invention.

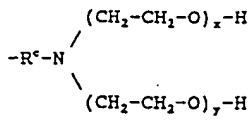
The use of hydroxyalkane oligocarboxylic acids as complexing agents in industrial alkaline cleaners is also known. For example, WO 92/08824 describes a water-containing alkaline cleaner for aluminium with a pH value of 10 to 12 which contains an alkaline builder component, aminoalkyl or hydroxyalkyl diphosphonic acids, surfactants and complexing agents for aluminium. Gluconates and tartrates inter alia are mentioned as complexing agents for aluminium. Hitherto unpublished German patent application P 42 32 612.5 describes the use of a combination of a phosphonic acid, an oxidizing agent and at least one short-chain organic carboxylic acid selected from inter alia tartaric acid and citric acid in acidic aqueous solutions with a pH value of 0 to 3 for the removal of magnetite coatings in water-carrying systems.

DE-A-36 03 579 describes acidic cleaning concentrates containing phosphoric acid in which ethoxylated fatty amines corresponding to general formula (V) are present as a key constituent:



(V)

In this formula,
n is an integer of 2 to 30,
R^a is a linear or branched, saturated or unsaturated alkyl radical containing 8 to 24 carbon atoms and R^b is a $-(CH_2-CH_2-O)_n-H$ group or a



group, where

R^5 is an alkylene radical containing 2 to 6 carbon atoms, m, x and y are each numbers of 0 to 30.

The concentrates also contain a combination of different phosphonic acids corresponding to general formulae I, II and III below and, in some cases, gluconic acid. The total phosphonic acid content is greater than the gluconic acid content.

German patent application P 43 24 396.7 describes cleaning formulations of high wetting power which are preferably used for cleaning plastic surfaces. They contain as key constituents monoamino- or diamino-mono- or -dicarboxylic acids or amides thereof in combination with relatively long-chain carboxylic acids and nonionic surfactants. These cleaners may contain as optional components hydroxypolycarboxylic acids, such as tartaric acid and citric acid, geminal diphosphonic acids, such as 1-hydroxyethane-1,1-diphosphonic acid, aminophosphonic acids and phosphonopolycarboxylic acids. These cleaners may also contain alkali metal hydroxides as builders.

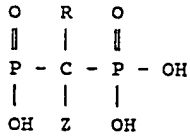
It has surprisingly been found a combination of hydroxyoligocarboxylic acids and phosphonic acids known as sequestrants in certain quantity ratios distinctly reduces the corrosion of glass caused by alkaline carbonate-containing cleaning solutions. The well-known complexing properties of these active substances had actually been expected to increase the corrosion rate.

In a first embodiment, the present invention relates to an additive in the form of an aqueous solution for addition to alkaline cleaning baths for the machine

washing of glass bottles, consisting of

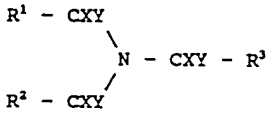
a) 7 to 25% by weight, based on the free acid, of one or more aliphatic hydroxymono-, hydroxydi- or hydroxytricarboxylic acids containing 2 to 6 carbon atoms and 1 to 5 hydroxy groups and/or aliphatic monoamino- or diamino-mono- or -dicarboxylic acids containing 2 to 6 carbon atoms or water-soluble salts thereof,

b) 1 to 12% by weight, based on the free acid, of one or more geminal disphosphonic acids corresponding to general formula (I):



(I)

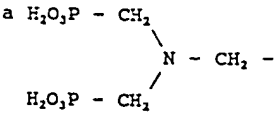
in which R is an alkyl radical containing 1 to 5 carbon atoms and Z is hydrogen, a hydroxy group or an amino group,
and/or one or more aminomethylene phosphonic acids corresponding to general formula (II):



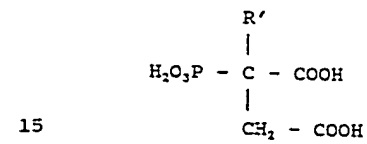
(II)

in which X and Y independently of one another represent hydrogen or an alkyl group containing 1 to 4 carbon atoms,
R^1 and R^2 represent $-PO_3H_2$ or a group corresponding to

the formula



and R^3 represents $-PO_3H_2$
and/or one or more phosphonocarboxylic acids corresponding to general formula (III):



(III)

in which R' is hydrogen, an alkyl group containing 1 to 4 carbon atoms or a $-CH_2-CH_2-COOH$ group, or water-soluble salts thereof,

c) 63 to 92% by weight of water or an aqueous solution of other auxiliaries,

the total concentration of the carboxylic acids of group a) being no lower than the total concentration of the phosphonic acids of group b).

The additive preferably contains 10 to 20% by weight, based on the free acid, of one or more of the carboxylic acids of group a) or water-soluble salts thereof and/or, preferably and, 2 to 6% by weight, based on the free acid, of one or more of the phosphonic acids of group b) or water-soluble salts thereof and 68 to 91% by weight and preferably 74 to 88% by weight of water or an aqueous solution of other auxiliaries.

Since the additive is intended for addition to an alkaline cleaning solution, the acids suitable for use in accordance with the invention are present in the in-use solution in the form of their anions irrespective of

whether the additive contains them as free acids or as water-soluble salts. If the carboxylic acids of group a) and/or the phosphonic acids of group b) are used as water-soluble salts, the alkali metal or ammonium salts are particularly suitable, sodium salts preferably being used. The expression "water-soluble" in this regard means that the salts are soluble in the aqueous phase of the additive in the concentration ranges mentioned above, based on the free acids.

Suitable hydroxycarboxylic acids of group a) are, in particular, hydroxyacetic acid, lactic acid, gluconic acid, tartronic acid, malic acid, tartaric acid and citric acid. Aminocarboxylic acids of group a) are also suitable for the purposes of the invention. The naturally occurring alpha-amino acids or amino acid derivatives are generally chiral in relation to the carbon atom carrying the amino group and are present in the L-form. Although the chiral L-amino acids do not afford any particular advantages for the technical application according to the invention, they are preferably used as natural active substances or as active substances identical with those occurring in nature. Accordingly, the following amino acids, for example, may be used in the form of their racemates or in optically active form: glycine, alanine, valine, leucine, isoleucine, beta-alanine, gamma-aminobutyric acid, epsilon-aminocaproic acid, glutamine, glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid and 2-amino-2-methylpentanedioic acid. The amino acids may additionally bear hydroxyl groups. Examples of corresponding amino acids are serine and threonine.

In one particularly advantageous embodiment, the additive contains 2 to 4 and preferably 3 different carboxylic acids, more especially hydroxycarboxylic acids of group a), the combination of gluconic acid, lactic

acid and citric acid leading to particularly positive results. In one favorable embodiment, the additive contains gluconic acid, lactic acid and citric acid or water-soluble salts thereof in a ratio by weight of 1 : (0.5 to 1.5) : (0.5 to 1.5) and preferably in a ratio by weight of 1 : (0.7 to 1.0) : (0.8 to 1.2).

Suitable phosphonic acids are mentioned in DE-C-23 25 829. Accordingly, the phosphonic acids of group b) or water-soluble salts thereof are preferably selected from the following groups:

formula (I): 1-aminoethane-1,1-diphosphonic acid and 1-hydroxyethane-1,1-diphosphonic acid,

formula (II): ethylenediamine tetramethylene phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, aminotri-(2-propylene-2-phosphonic acid), aminotrimethylene phosphonic acid,

formula (III): phosphonosuccinic acid, methyl phosphonosuccinic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid.

In another advantageous embodiment, the additive contains phosphonic acids or water-soluble salts thereof corresponding to general formula (I) and/or (III), at least one phosphonic acid corresponding to each of formulae (I) and (III), more especially 1-hydroxyethane-1,1-diphosphonic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid, preferably being used.

A preferred additive is characterized in that it contains a phosphonic acid or water-soluble salts thereof corresponding to each of general formulae (I) and (III) in a ratio by weight of 1:10 to 10:1, preferably in a ratio by weight of 1:1 to 10:1 and more preferably in a

ratio by weight of 6:1 to 9:1.

It has proved to be of advantage to establish certain ratios by weight between the total content of carboxylic acids of group a) and the total content of phosphonic acids of group b). Particularly favorable glass corrosion values were observed when the ratio by weight of the carboxylic acids of group a) to the phosphonic acids of group b) is in the range from 1:1 to 5:1 and preferably in the range from 2:1 to 4:1.

The effect according to the invention is actually achieved when the additive contains only water besides the above-mentioned components from groups a) and b). Depending on the application conditions, however, it can be of advantage to add other auxiliaries to the water phase of the additive. These include in particular defoamers to control the foam which is often formed in the washing of glass bottles containing proteinaceous soils. Accordingly, a defoamer solution is preferably used as the aqueous solution c), in which case it is recommended in accordance with the invention that the defoamer should make up from 1 to 25% by weight, preferably from 10 to 20% by weight and more preferably from 13 to 18% by weight of the additive as a whole.

The defoamer may be empirically selected according to the types of soil on the glass bottles. Polyglycol ethers of the type recommended in EP-B-124 815 as foam-suppressing additives in low-foam cleaning formulations have been successfully used. Accordingly, the defoamer is preferably selected from the group of polyethylene glycol ethers corresponding to general formula (IV):

$$R^4\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}R^3 \qquad \text{(IV)}$$

in which R^4 is a linear or branched alkyl or alkenyl radical containing 8 to 18 carbon atoms, n is a number of

7 to 12 and preferably 8 to 10 and R^3 is an alkyl radical containing 4 to 8 carbon atoms and more especially 4 carbon atoms.

It is known that other surface-active auxiliaries, for example those having a favorable effect on the separation behavior of labels, can be added to the cleaning solutions for bottle washing machines. Nonionic surfactants based on ethoxylation and/or propoxylation products of fatty alcohols or fatty amines can be used for this purpose. A particularly suitable group of products based on ethoxylated fatty amines is described in the above-cited DE-A-36 03 579. The fatty amine ethoxylates described therein are also suitable as auxiliaries for increasing the cleaning performance of the additives according to the invention. Reaction products of fatty amines containing 10 to 18 carbon atoms with 8 to 16 moles of ethylene oxide are particularly suitable as surface-active auxiliaries. In one favorable embodiment, the nonionic surfactant(s) is/are present in the aqueous solution c) in such a quantity that they make up from 1 to 6% by weight and preferably from 2 to 4% by weight of the additive as a whole.

The polyether chain - obtained by alkoxylation - of the defoaming and surface-active auxiliaries may be present in the conventional homolog distribution or in the so-called "narrow-range" homolog distribution. One method of producing narrow-range alkoxylation products is described, for example, in DE-A-38 43 713.

In order to facilitate analysis and establishment of the concentration of active substances in the cleaning bath, it is helpful if the ready-to-use cleaning solution or the concentrated additive therefor contains tracer substances readily determinable by analysis. One example of such a tracer substance is a soluble iodide, more especially potassium iodide, of which the content in the

bath solution may readily be determined by iodometric titration. Accordingly, the additive preferably contains such a tracer substance in a concentration which can readily be determined in the dilute bath solution, but which does not lead to applicational or wastewater problems. For example, the additive according to the invention may contain 0.1 to 0.5% by weight of potassium iodide.

In another embodiment, the invention relates to the use of the additive in an aqueous cleaning solution containing alkali metal hydroxide for the machine washing of glass bottles. The use according to the invention is characterized in that the cleaning solution has a content of active substances which can be adjusted by adding the additive described above to the cleaning solution in such quantities that the content of carboxylic acids of group a) in the cleaning solution is from 100 to 1,000 mg/l, preferably from 200 to 800 mg/l and more preferably from 300 to 600 mg/l while the content of phosphonic acids of group b) is from 50 to 400 mg/l and preferably from 75 to 200 mg/l. The NaOH content of the cleaning solution is in the usual range of 0.5 to 5% by weight and preferably 1 to 3% by weight.

In one advantageous embodiment of the use according to the invention, the additive described above, which is formulated as a concentrate of active substances, is added in the appropriate dosage to the cleaning solution containing alkali metal hydroxide. However, the individual active substances may of course also be separately added to the cleaning solution in the concentration ranges mentioned above. By comparing the concentrations of the active substances of groups a) and b) in the final cleaning solution and in the additive, it is readily possible to calculate the concentrations of the other auxiliaries, nonionic surfactants, defoamers and tracers

established by corresponding dilution of the additive.

The use according to the invention is further characterized in that the bottles are contacted with the cleaning solution over a period of 1 to 30 minutes and preferably over a period of 3 to 20 minutes at temperatures of 40 to 90°C and preferably at temperatures of 55 to 85°C.

Examples

The invention is illustrated by the following Examples. To determine the relative corrosion rate of glass bottles with cleaning solutions according to the invention and with comparison solutions, new 0.33 liter glass bottles (so-called Vichy bottles) were immersed in the particular solutions for 24 hours at 80°C and the weight loss was determined in grams of material removed per bottle. Even though these experimental conditions do not correspond to the conditions prevailing in an industrial bottle washing plant, the relative corrosive effect of the individual solutions can nevertheless be determined.

In order to standardize the conditions, the test solutions (except for comparison 1) contained 2% by weight of sodium carbonate to simulate the conditions prevailing in industrial baths. In practice, the sodium carbonate content of the cleaning solutions is subject to significant variation. All the test solutions contained 2.5% by weight of NaOH, the components listed in Table 1 and water to 100%. Comparison solution 1 was carbonate-free.

The test results are set out in Table 1.

Examples 14 to 18

Additive concentrates were prepared in the form of aqueous solutions for addition to aqueous alkaline

Legend to Table 1

*)A) Gluconic acid
B) Lactic acid
C) Citric acid
D) Glycine
E) Glutamic acid
F) 2-Phosphonobutane-1,2,4-tricarboxylic acid
G) 1-Hydroxyethane-1,1-diphosphonic acid
H) Aminotrimethylene phosphonic acid
I) Fatty alcohol x 9.6 ethylene oxide butyl ether (Dehypon® LT104, Henkel KGaA)
K) Cocoamine x 12 ethylene oxide

Canadian Patent Database

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Patent Document Number 2176336 :
ADDITIVE FOR USE IN GLASS-BOTTLE WASHING AND ITS USE IN DECREASING GLASS CORROSION

ADJUVANT POUR LE LAVAGE DES BOUTEILLES EN VERRE ET SON UTILISATION POUR REDUIRE LA CORROSION DU VERRE

CLAIMS:

Replacement Claims

1. An additive in the form of an aqueous solution for addition to alkaline cleaning baths for the machine washing of glass bottles, consisting of
a) 7 to 25% by weight, based on the free acid, of one or more aliphatic hydroxymono-, hydroxydi- or hydroxytricarboxylic acids containing at least 2 and up to 6 carbon atoms and 1 to 5 hydroxy groups and/ or aliphatic monoamino-monocarboxylic acids or dicarboxylic acids or diamino-monocarboxylic acids or -dicarboxylic acids containing at least 2 and up to 6 carbon atoms or water-soluble salts thereof,
b) 1 to 12% by weight, based on the free acid, of one or more geminal disphosphonic acids corresponding to general formula (I):
image (I) in which R is an alkyl radical containing 1 to 5 carbon atoms and Z is hydrogen a hydroxy group or an amino group, and/or one or more aminomethylene phosphonic acids corresponding to general formula (II):
image (II) in which X and Y independently of one another represent hydrogen or an alkyl group containing 1 to

4 carbon atoms, R1 and R2 represent -PO3H2 or a group corresponding to the formula

[Image] and R3 represents -PO3H2 and/or one or more phosphonocarboxylic acids corresponding to general formula (III):
[Image] (III) in which R' is hydrogen, an alkyl group containing

1 to 4 carbon atoms or a -CH2-CH2-COOH group, or water-soluble salts thereof,
c) 63 to 92% by weight of water or an aqueous solution of other auxiliaries, the total concentration of the carboxylic acids of group
a) being no lower than the total concentration of the phosphonic acids of group b).

2. An additive as claimed in claim 1, characterized in that it consists of

10 to 20% by weight, based on the free acid, of one or more of the carboxylic acids of group a) or water-soluble salts thereof and

2 to 6% by weight, based on the free acid, of one or more of the phosphonic acids of group b) or water-soluble salts thereof and

74 to 88% by weight of water or an aqueous solution of other auxiliaries.

3. An additive as claimed in one or both of claims 1 and 2, characterized in that alkali metal or ammonium salts, preferably sodium salts, are used as the watersoluble salts of the carboxylic acids of group a) and/or the phosphonic acids of group b).

4. An additive as claimed in one or more of claims 1 to

3, characterized in that the hydroxycarboxylic acids of group a) are selected from hydroxyacetic acid, lactic acid, gluconic acid, tartronic acid, malic acid, tartaric acid and citric acid.

5. An additive as claimed in one or more of claims 1 to

3, characterized in that the aminocarboxylic acids of group a) are selected from glycine, alanine, .beta.-alanine, valine, leucine, isoleucine, .gamma.-aminobutyric acid, .epsilon.aminocaproic acid, glutamine, glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid and 2-amino-2-methylpentanedioic acid.

6. An additive as claimed in one or more of claims 1 to

3, characterized in that the amino acids of group a) carry additional hydroxyl groups and are preferably selected from serine and threonine.

7. An additive as claimed in one or more of claims 4 to

6, characterized in that it contains 2 to 4. and preferably 3 different carboxylic acids, preferably hydroxycarboxylic acids, more particularly gluconic acid, lactic acid and citric acid, or water-soluble salts thereof.

8. An additive as claimed in claim 7, characterized in that it contains gluconic acid, lactic acid and citric acid or water-soluble salts thereof in a ratio by weight of 1: (0.5 to 1.5): (0.5 to 1.5) and preferably in a ratio by weight of 1 : (0.7 to 1.0) : (0.8 to 1.2).

9. An additive as claimed in one or more of claims 1 to

8, characterized in that the phosphonic acids of group b) or water-soluble salts thereof are selected from the following groups: formula (I): 1-aminoethane-1,1-diphosphonic acid and 1hydroxyethane-1,1-diphosphonic acid, formula (II): ethylenediamine tetramethylene phosphonic acid, diethylenetriamine pentamethylene phosphonic acid, aminotri-(2-propylene-2-phosphonic acid), aminotrimethylene phosphonic acid, formula (III): phosphonosuccinic acid, methyl phosphonosuccinic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid.

10. An additive as claimed in claim 9, characterized in that it contains phosphonic acids or water-soluble salts thereof corresponding to general formula (I) and/or (III), at least one phosphonic acid corresponding to each of formulae (I) and (III), more especially 1-hydroxy-ethane-1,1-diphosphonic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid, preferably being used.

11. An additive as claimed in claim 10, characterized in that it contains a phosphonic acid or water-soluble salts thereof corresponding to each of general formulae (I) and (III) in a ratio by weight of 1:10 to 10:1, preferably in a ratio by weight of 1:1 to 10:1 and more preferably in a ratio of 6:1 to 9:1.

12. An additive as claimed in one or more of claims 1 to

11, characterized in that the ratio by weight of the carboxylic acids of group a) to the phosphonic acids of group b) is 1:1 to 5:1 and preferably 2:1 to 4:1.

13. An additive as claimed in one or more of claims 1 to

12, characterized in that a defoamer solution is used as the aqueous solution c).

14. An additive as claimed in claim 13, characterized in that the defoamer makes up from 1 to 25% by weight, preferably 10 to 20% by weight and more preferably 13 to

18% by weight of the additive as a whole.

15. An additive as claimed in one or both of claims 13 and 14, characterized in that the defoamer is selected from the group of polyethylene glycol ethers corresponding to general formula (IV):
R4-O-(CH2-CH2-O)n-R5 (IV) in which R4 is a linear or branched alkyl or alkenyl radical containing 8 to 18 carbon atoms, n is a number of

7 to 12 and preferably 8 to 10 and R5 is an alkyl radical containing 4 to 8 carbon atoms and more especially 4 carbon atoms.

16. An additive as claimed in one or more of claims 1 to

15, characterized in that the aqueous solution c) additionally contains one or more nonionic surfactants based on ethoxylation and/or propoxylation products of fatty alcohols or fatty amines, preferably ethoxylation products of fatty amines, more especially reaction products of fatty amines containing 10 to 18 carbon atoms with 8 to 16 moles of ethylene oxide, the nonionic surfactant(s) making up from 1 to 6% by weight and preferably from 2 to

4% by weight of the additive as a whole.

17. The use of the additive claimed in one or more of claims 1 to 16 for reducing the corrosion of glass in aqueous cleaning solutions for bottle washing machines having an alkali metal hydroxide content of 0.5 to 5% by weight and preferably 1 to 396 by weight, characterized in that the cleaning solutions have a content of active substances which can be adjusted by adding the additive to the cleaning solution in such quantities that the content of carboxylic acids of group a) in the cleaning solution is from 100 to 1,000 mg/l, preferably from 200 to 800 mg/l and more preferably from 300 to 600 mg/l and the content of phosphonic acids of group b) is from 50 to

400 mg/l and preferably from 75 to 200 mg/l.

18. The use claimed in claim 17, characterized in that the bottles are contacted with the cleaning solution for

1 to 30 minutes and preferably for 3 to 20 minutes at temperatures of 40 to 90°C and preferably at temperatures of 55

to 85°C.

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CA 2176336	AA 19950518	CA 2176336	A	19941103
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